THE EFFECTS OF PYROLYSIS CONDITIONS AND COAL TYPE
ON THE NATURE OF WATER-SOLUBLE ORGANIC EFFLUENTS

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Abstract

The effects of pyrolysis conditions and coal type on the nature of water-soluble organic effluents have been investigated using a small pyrolysis reactor with a helium atmosphere at ambient pressure and a sample size of five grams. The reactor is capable of a maximum heating rate of 45°C/min and a maximum furnace temperature of 1100°C. Variables examined include: 1) particle size, 2) maximum temperature, 3) time at temperature, and 4) heating rate. Six coals of various rank were investigated. In addition, three lithotypes of the same coal were examined.

Introduction

The treatment and removal of water-soluble organic effluents from wastewater is an important issue facing coal gasification technology. The extent of treatment is governed by the reuse or environmentally acceptable disposal of the wastewater. Downstream effluent treatment is also dependent on the nature and quantity of tars and water-soluble organics which are produced by pyrolysis and devolatilization reactions in the upper portion of the gasifier. It is desirable to develop a laboratory test to simulate the production of water-soluble organic effluents from a gasifier, thereby eliminating expensive pilot plant tests. Such a test would allow for the prediction of waste composition from specific coals at a variety of operating conditions.

Experimental

A laboratory scale tubular reactor was constructed which allows for the pyrolysis of up to five grams of coal in an inert atmosphere. A Lindbergh split-type furnace with a maximum temperature of 1100°C and programmable heating rate of 5°C/min. to 45°C/min. has been used for heating. A liquid nitrogen cooled trap is used for the collection of water-soluble organic effluents. After completion of the experiment the trap is allowed to warm to above 0°C and the water-soluble organics analyzed by gas chromatography (1). The six coals used in this study with their proximate and ultimate analyses are listed in Table I.

Table I. Coal Sample Bank Analysis for Six Coals.

	Indian Head	Gascoyne Blue	Rosebud	Center	Sufco	Illinois Seam No.6
Proximate Analysis, as rec'd; % by wt.						
Moisture	34.0	32.2	25.0	34.7	9.6	2.9
Volatile matter	27.4	34.2	28.6	28.1	33.9	37.3
Fixed carbon*	33.8	17.6	39.2	31.7	48.0	48.6
Ash	4.8	6.0	7.1	5.5	8.5	11.2
Ultimate Analysis maf; % by wt.						
Hydrogen	4.18	5.69	5.11	4.51	5.25	5.54
Carbon	72.03	59.77	76.27	69.97	79.20	77.19
Nitrogen	1.05	0.92	1.28	1.24	1.43	1.61
Sulfur	0.62	1.49	0.93	1.27	0.51	4.59
Oxygen*	22.13	32.12	16.37	23.01	13.61	11.08
Rank	Lig.	Lig.	Subbit.	Lig.	Bit.	Bit.

*By difference.

Results and Discussion

Effect of Coal Type on the Nature of Water-Soluble Organic Effluents

To develop a correlation between water-soluble organic effluent yields and coal type, six different coals were pyrolyzed in the small pyrolysis reactor (SPR) under identical conditions. The pyrolysis conditions used were a heating rate of 45°C/min., a maximum temperature of 850°C, helium atmosphere, -60 mesh particle size, and a sample size of approximately 5 grams. The data (Table II) indicate water-soluble organic effluent yields to be dependent on coal type, with all products showing significant variation.

467

Table II. Yields of Water-Soluble Organic Effluents for a Variety of Coal Types.*

Compound	Indian Head	Gascoyne Blue	Rosebud	Center	Sufco	Illinois Seam No. 6
Methanol	1490	730	40	1700	10	40
Acetone	1420	1600	930	1480	750	500
Acetonitrile	230	220	180	280	100	140
2-Butanone	400	510	320	440	250	120
Propionitrile	130	230	90	370	50	40
Phenol	2300	2900	3000	3440	920	1720
o-Cresol	510	590	850	780	390	740
p-Cresol	760	1080	1290	1360	400	950
m-Cresol	710	910	1290	1400	510	1190

*Yields are reported in micrograms/g maf coal.

Effect of Lithotype Composition on the Yields of Water-Soluble Organic Effluents

Several small pyrolysis reactor runs were performed using durain, fusain, and vitrain lithotypes from 8eulah high-sodium (ND) lignite. The pyrolysis conditions used were: a heating rate of 45°C/min., final temperature of 850°C, helium atmosphere and a sample size of approximately five grams. The data (Table III) reveal lithotype-specific variation for most compounds, with the greatest variations in yields being for methanol, acetone, phenol, cresols, and catechol. The vitrain lithotype produced nearly three times the amount of total pyrolysis products as the durain lithotype, suggesting that petrologic analysis of coal samples might be useful in predicting wastewater composition. These results also suggest that petrologic variations within a seam might produce significant variations in wastewater composition as coal mined from different parts of the same seam is gasified.

Table III. Yields of Water-Soluble Organic Effluents for Three Lithotypes.*

Compound	Vitrain	Durain	Fusain
Methanol	2680	580	730
Acetone	1910	1340	1390
Acetonitrile	280	310	270
2-Butanone	480	380	380
Propionitrile	110	160	370
Phenol	2680	1690	3040
o-Cresol	590	340	780
p-Cresol	720	460	850
m-Cresol	680	420	880
Catechol	6940	990	1010

*Yields are reported in micrograms/g maf coal.

Correlation of Yields of Water-Soluble Organic Effluents to Coal Parameters

It is the ultimate goal of this project to develop a series of equations which will predict wastewater composition from a gasifier based, in part, on certain coal parameters easily determined in the laboratory. Relationships have been found which correlate the yields of three pyrolysis products, methanol, 2-butanone and acetone, to coal-specific data which is readily available.

Methoxy content determinations (2) have been made for eleven different samples tested in the small pyrolysis reactor. These samples include whole coals as well as individual lithotypes. The methoxy contents of the lithotypes were plotted versus the yield of methanol generated during pyrolysis to 850°C. A linear least squares fit of the data resulted in a correlation coefficient of 0.95.

The yields of 2-butanone and acetone were plotted versus carbon/oxygen ratios for six coals pyrolyzed in the small pyrolysis reactor. A linear least squares fit of the data gave a very good fit for both compounds (Figure 1 and Figure 2). 2-Butanone and acetone both had correlation coefficients of 0.99.

Future work will focus on the identification of further relationships which will attempt to correlate pyrolysis yields of the remaining six compounds with other coal parameters.

Effect of Pyrolysis Conditions on the Nature of Water-Soluble Organic Effluents

Effect of Particle Size. In order to determine the effect of particle size on the yield of water-soluble organic effluents, the pyrolysis products from -60 mesh coal were compared to the products from 1/2 inch particles for Rosebud (MT) coal. The pyrolysis conditions were a heating rate of 45°C/min., final temperature 850°C, and a helium atmosphere. The effect of particle size was negligible; the yield of water-soluble organic effluents was independent of the size of the coal particle which generated those effluents (Table IV). However, it is advantageous to use riffled -60 mesh coal particles in most experiments in order to avoid inhomogeneity in the coal sample, which would result in anomalous effluent yields.

Table IV. Effect of Coal Particle Size on the Nature of Water-Soluble Organic Effluent.*

Compound	Rosebud	
	-60 mesh	1/2 inch
Methanol	40	30
Acetone	930	890
Acetonitrile	180	160
2-Butanone	320	320
Propionitrile	90	30
Phenol	3000	2810
o-Cresol	850	850
o-Cresol	1290	1220
m-Cresol	1290	1230

*Reported as micrograms/g maf coal.

Effect of Maximum Temperature. To determine the effect of maximum temperature on the yield of water soluble organic effluents, Indian Head (ND) lignite was pyrolyzed at two final temperatures: 850° and 1100°C. The pyrolysis conditions used were a heating rate of 45°C/min., -60 mesh particle size, and a sample size of approximately 5 grams. A comparison of the yield data (Table V) for these two runs revealed the yields of methanol, acetone, acetonitrile, 2-butanone and propionitrile to be similar. However, the increased yields of phenol and cresols at 1100°C suggest that the evolution of water-soluble organics is not complete at 850°C. Model studies indicate that phenol and cresols generated at the lower temperatures evolve from alkyl-aryl ether precursors (3). The increase in phenol and cresol yields at 1100°C may result, in part, from the cleavage of diaryl ethers with their relatively higher carbon-oxygen bond energies.

Table V. Effect of Maximum Temperature on the Nature of Water-Soluble Organic Effluents.

Compound	Micrograms/g maf coal	
	850°C	1100°C
Methanol	1490	1460
Acetone	1420	1490
Acetonitrile	230	240
2-Butanone	400	400
Propionitrile	130	90
Phenol	2300	3220
o-Cresol	510	740
p-Cresol	760	1120
m-Cresol	710	1270

Effect of Time at Temperature. Indian Head (ND) and Rosebud (MT) coals were subjected to zero and 30 minute isothermal periods at maximum temperatures of 380°C and 850°C to determine the effect of time at temperature ("residence time") on pyrolysis yields for water-soluble organics. The pyrolysis conditions were a heating rate of 45°C/min., a helium atmosphere, and a sample size of approximately 5 grams. The effect of residence time on the yields of water-soluble organics (Table VI) was substantial at 380°C. With no isothermal period, the yield of products was below the gas chromatograph's threshold for accurate quantification. At the higher temperature the effect of residence time was quite small and in the case of the Indian Head lignite nonexistent.

Table VI.   Effect of Time at Temperature on the Nature of Water-Soluble Organic Effluents.*

| | Maximum Temperature 380°C | | | |
| | Indian Head | | Rosebud | |
Compound	0 min.	30 min.	0 min.	30 min.
Methanol	**	900	**	20
Acetone	**	480	**	300
Acetonitrile	**	30	**	10
2-Butanone	**	140	**	130
Propionitrile	**	**	**	10
Phenol	**	1370	**	540
o-Cresol	**	350	**	120
p-Cresol	**	550	**	230
m-Cresol	**	450	**	170
Catechol	**	1480	---	---

| | Maximum Temperature 850°C | | | |
| | Indian Head | | Rosebud | |
Compound	0 min.	30 min.	0 min.	30 min.
Methanol	1490	1740	40	30
Acetone	1420	1460	930	840
Acetonitrile	230	240	180	170
2-Butanone	400	370	320	280
Propionitrile	130	270	90	20
Phenol	2300	2360	3000	2690
o-Cresol	510	530	850	800
p-Cresol	760	820	1290	1080
m-Cresol	710	820	1290	1140
Catechol	2210	2120	---	---

  *Reported in micrograms/g maf coal.
 **Below instrument threshold for accurate quantification.
---Not determined.

Effect of Heating Rate.   To determine the effect of heating rate on the yield of water-soluble organic effluents, pyrolysis of Center Mine (ND) lignite was carried out at 380°C and 850°C using heat rates of 5°C/min. and 45°C/min.   Both the 380°C data and the 850°C data (Table VII) reveal a higher yield for phenol and cresols at the slower heating rate.   This could be due to the relative length of the experiments; the fast heating rate experiment takes approximately 20 minutes, whereas the slow heating rate experiment takes 170 minutes.   It is possible that the effect that is being observed is not so much heating rate as it is time at temperature ("residence time").

Table VII. Effect of Heating Rate on the Nature of Water-Soluble Organic Effluents.*

Compound	380 Maximum Temp.		850 Maximum Temp.	
	5°C/min.	45°C/min.	5°C/min.	45°C/min.
Methanol	570	270	1590	1700
Acetone	110	40	1190	1490
Acetonitrile	**	**	300	280
2-Butanone	20	10	310	440
Propionitrile	**	**	30	380
Phenol	460	100	4380	3460
o-Cresol	50	10	1300	780
p-Cresol	180	40	1740	1360
m-Cresol	80	10	1920	1400

*Results are reported in micrograms/g maf coal.
**Below instrument threshold for accurate quantification.

Conclusion

A laboratory scale tubular reactor test is able to differentiate between the relative yields of several water-soluble organic effluents produced during pyrolysis for a variety of coals under differing pyrolysis conditions. Correlations between pyrolysis yields and certain coal parameters for three of the compounds examined have been developed which allow for the prediction of pyrolysis yields for these compounds for as yet untested coals.

Acknowledgment

Literature Cited

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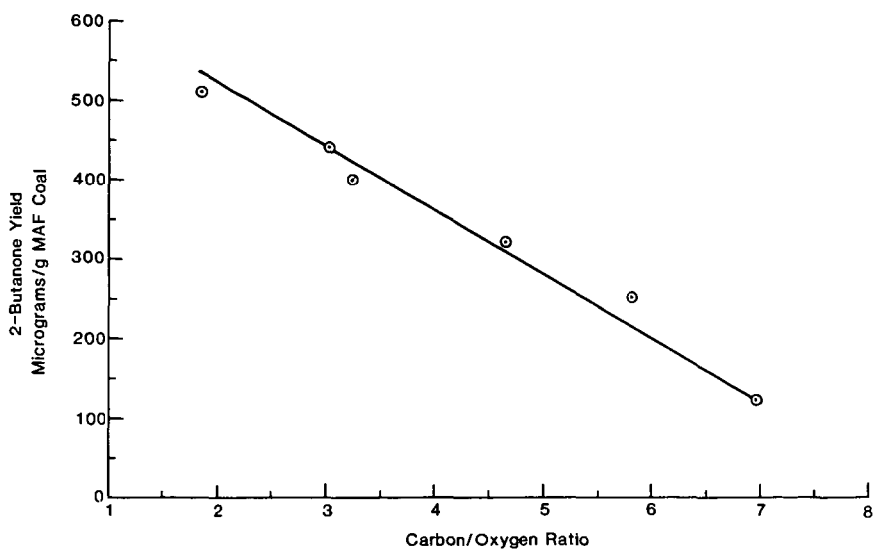3. Siskin, Michael and Thomas Aczel, Fuel, 62, 1321 (1983).

Figure 1.   Correlation of 2-butanone yields to carbon/oxygen ratio for the six coals listed in Table I.
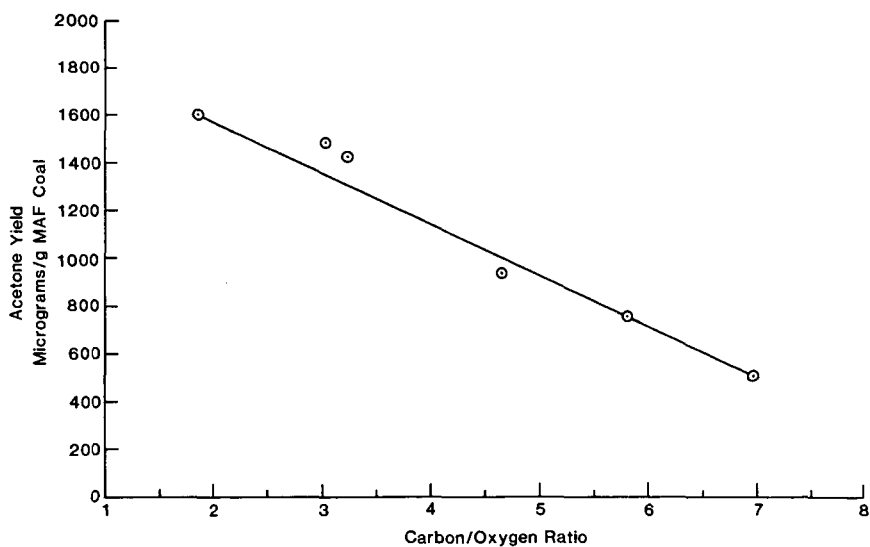

Figure 2.   Correlation of acetone yields to carbon/oxygen ratio for the six coals listed in Table I.

473